

hedral for the green complex to planar for the yellow complex. Recently an X-ray structure determination of solid single crystals of nickel-tetraglycine complex shows that the nickel ion is coordinated to the four available nitrogen centers arranged in a plane while the carboxylate group remains free.¹⁷ This corresponds closely to the suggested structure for nickel triglycine with the carboxylate group in place of one of the nitrogens in the tetraglycine complex. An X-ray structure determination of nickel diethylenediaminomalonate, which shows a color change behavior similar to that of nickel triglycine, confirms that in this complex the nickel ion is again planar.¹⁸

Comparing the copper and nickel complexes of di- and triglycine reveals that the driving force in the dis-

(19) R. M. Lewis, private communication.

sociation of the peptide hydrogen from the complexes appears to be intimately related to the strength of the bond formed between the two metals with the ligands. Thus the copper complexes are formed with greater exothermic enthalpy changes than the nickel complexes, and correspondingly the dissociation of the peptide hydrogen from the copper complexes occurs at lower pH than the nickel analog. In the diglycine case the dissociation occurs only from the bis complex suggesting that the formation of a mono complex is insufficient to compensate energetically for the dissociation of a proton from the peptide group. It is also reasonable to assume that the resulting change of coordinating centers from oxygen to nitrogen favors the copper ion as compared with the nickel ion in view of the higher copper-amine bond energy.

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Spectral and Magnetic Behavior of Some Cobalt(II) and Nickel(II) Complexes Involving Coordination by the Halo Group

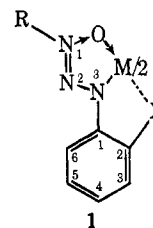
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Halo groups attached to benzene rings are capable of occupying coordination positions in some triazene 1-oxide complexes of the general structure 1. On the basis of comparisons of magnetic moments and electronic spectra of the various complexes with those of one cobalt(II) complex of definitely known structure it is concluded that all the cobalt(II) complexes except one ($X = I$) are pseudooctahedral both in the solid state and in the solution phase (benzene) in which the complexes are monomeric. The iodo complex is grossly planar in the crystalline state but becomes pseudooctahedral in the solution phase. All the pseudooctahedral complexes show splittings of the ν_1 crystal field band. The splittings (which follow the orders $F < Cl < Br < I$ and $OCH_3 < SCH_3$) are attributed to the low symmetry of the ligand field. In this class of complexes, the octahedral quartet state of cobalt(II) is more readily achieved than the octahedral triplet state of nickel(II). Among nickel(II) complexes, those having $X = OCH_3, OC_2H_5,$ and SCH_3 show magnetic moments and electronic spectra typical of a distorted octahedral geometry both in solid and in solution. On the other hand, nickel(II) complexes with $X =$ halogen are diamagnetic in the crystalline state but become partially paramagnetic in the solution phase. On the basis of spectral and magnetic data it is shown that planar ($S = 0$) \rightleftharpoons pseudooctahedral ($S = 1$) equilibria exist in these solutions. The pseudooctahedral form involves halogen coordination. The population of the octahedral configuration follows the order $F < Cl < Br > I$. The parameters ΔH° (and ΔS°) for the equilibria are found to be positive. A possible rationalization is discussed on the basis of a simple model.

Introduction

Triazene 1-oxides act as versatile ligands forming nonelectrolytic chelates with many metal ions.^{1,2} However, there is a surprising paucity of data on structural aspects of these extremely interesting complexes. The syntheses, stereochemistry, and electronic spectra of some cobalt(III),³ rhodium(III),⁴ and chromium(III)⁴ chelates derived from bidentate triazene 1-oxides were reported recently from this laboratory. All these complexes have a *trans*- MN_3O_3 coordination sphere. In this paper complexes of the structural type 1 are characterized using spectroscopic and magnetic data. In 1 the dotted line indicates that the donor group X may or may not be coordinated to the central metal atom. In what follows, the complexes 1 will be abbreviated as $(RX)_2M$.



R = CH₃, C₂H₅, n-C₃H₇
X = F, Cl, Br, I, OCH₃, OC₂H₅, SCH₃
M = Co, Ni

Experimental Section

Preparation of Compounds.—The ligands were synthesized by treating the appropriate diazonium salts with substituted hydroxylamines.³ The complexes were prepared as crystalline solids by treating an ethanolic or methanolic solution of the ligand (0.02 mol) with an aqueous or methanolic solution of the appropriate metal acetate (0.01 mol). In the case of $(CH_3F)_2Co$ the reaction was carried out under nitrogen. Recrystallizations were done from acetone.

- (1) M. Elkins and L. Hunter, *J. Chem. Soc.*, 1346 (1938).
- (2) D. N. Purohit, *Talanta*, **14**, 353 (1967).
- (3) A. Chakravorty, B. Behera, and P. S. Zacharias, *Inorg. Chim. Acta*, **2**, 85 (1968).
- (4) B. Behera and A. Chakravorty, *J. Inorg. Nucl. Chem.*, **31**, 1791 (1969).

TABLE I
 CHARACTERIZATION OF COBALT(II) AND NICKEL(II) COMPOUNDS OF TYPE 1^a

Compound			Formula	Mp, ^b °C	% C		% H		% N	
R 1	X 2	M 3			Calcd 6	Found 7	Calcd 8	Found 9	Calcd 10	Found 11
CH ₃	F	Co	C ₁₄ H ₁₄ N ₆ F ₂ O ₂ Co	159-160	42.56	42.31	3.55	3.30	21.30	21.62
CH ₃	Cl	Co	C ₁₄ H ₁₄ N ₆ Cl ₂ O ₂ Co	153-154	39.26	39.49	3.27	3.21	19.63	19.62
CH ₃	Br	Co	C ₁₄ H ₁₄ N ₆ Br ₂ O ₂ Co	135-137	32.52	32.11	2.71	2.44	16.26	16.06
CH ₃	I	Co	C ₁₄ H ₁₄ N ₆ I ₂ O ₂ Co	154-155	27.51	27.32	2.29	2.35	13.75	13.50
CH ₃	OCH ₃	Co	C ₁₆ H ₂₀ N ₆ O ₄ Co	192-193	45.83	45.86	4.77	4.89	20.06	20.40
CH ₃	OC ₂ H ₅	Co	C ₁₈ H ₂₄ N ₆ O ₄ Co	164-165	48.34	48.16	5.37	5.37	18.79	19.00
CH ₃	SCH ₃	Co	C ₁₆ H ₂₀ N ₆ S ₂ O ₂ Co	174-176	42.60	42.58	4.44	4.53	18.62	19.02
C ₂ H ₅	OCH ₃	Co	C ₁₈ H ₂₄ N ₆ O ₃ Co	147-148	48.43	48.90	5.37	5.28	18.79	18.76
C ₂ H ₅	OC ₂ H ₅	Co	C ₂₀ H ₂₈ N ₆ O ₄ Co	152-153	50.54	50.49	5.89	5.90	17.69	17.85
<i>n</i> -C ₃ H ₇	OCH ₃	Co	C ₂₀ H ₂₈ N ₆ O ₄ Co	112-113	50.56	50.90	5.90	5.72	17.70	17.86
CH ₃	F	Ni	C ₁₄ H ₁₄ N ₆ F ₂ O ₂ Ni	207-209	42.56	42.72	3.55	3.41	21.30	21.46
CH ₃	Cl	Ni	C ₁₄ H ₁₄ N ₆ Cl ₂ O ₂ Ni	175-176	39.28	39.79	3.27	3.30	19.64	19.73
C ₂ H ₅	Cl	Ni	C ₁₆ H ₁₈ N ₆ Cl ₂ O ₂ Ni	145-147	42.13	42.86	3.95	3.80	18.44	18.49
CH ₃	Br	Ni	C ₁₄ H ₁₄ N ₆ Br ₂ O ₂ Ni	179-180	32.52	31.93	2.71	2.82	16.26	16.02
CH ₃	I	Ni	C ₁₄ H ₁₄ N ₆ I ₂ O ₂ Ni	205-206	27.51	27.88	2.29	2.33	13.75	13.77
CH ₃	OCH ₃	Ni	C ₁₆ H ₂₀ N ₆ O ₄ Ni	211-213	45.85	45.71	4.78	4.86	20.01	20.40
CH ₃	OC ₂ H ₅	Ni	C ₁₈ H ₂₄ N ₆ O ₄ Ni	187-188	48.37	47.80	5.37	5.12	18.80	19.20
CH ₃	SCH ₃	Ni	C ₁₆ H ₂₀ N ₆ S ₂ O ₂ Ni	195-197	42.60	42.70	4.44	4.63	18.62	18.90
C ₂ H ₅	OCH ₃	Ni	C ₁₈ H ₂₄ N ₆ O ₄ Ni	136-138	48.37	48.40	5.37	5.23	18.80	18.44
C ₂ H ₅	OC ₂ H ₅	Ni	C ₂₀ H ₂₈ N ₆ O ₄ Ni	130-131	50.56	51.10	5.90	5.70	17.70	18.09
<i>n</i> -C ₃ H ₇	OCH ₃	Ni	C ₂₀ H ₂₈ N ₆ O ₄ Ni	127-128	50.56	50.42	5.89	5.60	17.70	18.03
CH ₃	H	Ni	C ₁₄ H ₁₄ N ₆ Cl ₂ Ni ^c	211-212	39.28	39.50	3.27	3.12	19.64	19.31
CH ₃	H	Ni	C ₁₆ H ₂₀ N ₆ O ₄ Ni ^d	130-131	45.85	45.72	4.78	4.56	20.06	20.43

^a Refer to the compound figure number in the text. ^b All melting points reported in this table are uncorrected. ^c Cl group in the 3 position of the benzene ring in 1. ^d OCH₃ group in the 3 position of the benzene ring in 1.

Electronic spectra were measured on a Cary 14 recording spectrophotometer. Solids were examined in Nujol mull. Variable-temperature solution measurements were done by circulating thermostated water through the cell holder. Bulk susceptibility measurements were carried out on a sensitive Guoy balance described elsewhere.⁵ CoHg(SCN)₄ and distilled water were used as standards for measurements on solids and solutions, respectively. Benzene used for solution measurements was carefully purified and then distilled over sodium. The gram-susceptibility of benzene was repeatedly found to be $-(0.703 \pm 0.003) \times 10^{-6}$ cgsu. Molecular weight measurements were carried out on a vapor pressure osmometer, Model 301A (Mechrolab Inc.), in benzene solution.

Results

Syntheses of Chelates.—As far as we know, all complexes reported in this paper are new. Characterization data for the chelates are shown in Table I. The synthetic procedure used is trivial and involves straightforward mixing of reagents. Only in the case of (CH₃F)₂Co, it is necessary to carry out the reaction under oxygen-free atmosphere. All crystalline complexes are stable in air. The chelates are soluble in a variety of organic solvents. In contrast to the unsubstituted (1, M = Co, X = H) complexes,^{1,6} the substituted cobalt(II) complexes described in this paper are in general remarkably stable to aerial oxidation in the solution phase.

Molecular Complexity in the Solution Phase.—In every case where measurements were made, the triazene 1-oxide chelates were found to be essentially monomolecular in benzene solution. Representative molecular weight results are as follows: (CH₃-OCH₃)₂Co, 410 (calcd 420); (CH₃Cl)₂Co, 427 (calcd 428); (CH₃OCH₃)₂Ni, 404 (calcd 419); (CH₃Cl)₂Ni, 434 (calcd 428); (C₂H₅Cl)₂Ni, 440 (calcd 456).

Magnetic Data.—Magnetic susceptibility data for a number of chelates in the solid state and in benzene solution are set out in Table II. The magnetic moments of all the cobalt(II) complexes except (CH₃I)₂Co

 TABLE II
 SELECTED MAGNETIC SUSCEPTIBILITY DATA^a
 ON COMPLEXES OF TYPE 1^b

Compound			μ_{eff} , BM	
R	X	M	Solid	Benzene soln ^c
CH ₃	F	Co	4.80	<i>d</i>
CH ₃	Cl	Co	4.85	4.70
CH ₃	I	Co	2.13	4.42
CH ₃	OCH ₃	Co	4.85	4.78
CH ₃	OC ₂ H ₅	Co	4.92	4.81
CH ₃	OCH ₃	Ni	3.25	3.21
CH ₃	OC ₂ H ₅	Ni	3.32	3.22
C ₂ H ₅	OCH ₃	Ni	3.27	<i>d</i>
CH ₃	SCH ₃	Ni	3.15	<i>d</i>

^a All measurements were done at room temperature (300-303°K). ^b Refer to compound figure number in the text. ^c Solution concentrations are in the range (3-4) $\times 10^{-2}$ M. ^d Measurements not made.

lie in the range 4.7-4.9 BM. The nickel(II) complexes having X = halogen are olive green and are uniformly diamagnetic in the crystalline state. However, the remaining nickel(II) complexes (X = OCH₃, OC₂H₅, SCH₃) are red to brown solids which are paramagnetic with μ_{eff} lying in the range 3.1-3.3 BM (Table II). In a few cases where measurements were made, the solution magnetic moments of the nickel(II) complexes were found to be close (Table II) to those of the crystalline complexes except for the complexes having X = halogen. These become partially paramagnetic in the solution phase and the paramagnetism is temperature dependent (Table III).

Electronic Spectra.—Some representative spectra of cobalt(II) complexes taken in Nujol mull and in benzene are shown in Figures 1 and 2, respectively. All spectral data for the cobalt(II) complexes are summarized in Table IV. The mull spectrum of the complex (CH₃Cl)₂Co shows two prominent features at 7300 and 11,360 cm⁻¹. In the bromo complex the separation of the two corresponding features increases whereas in the fluoro complex the two features ap-

(5) T. S. Kannan and A. Chakravorty, *Inorg. Chem.*, **9**, 1153 (1970).

(6) B. Behera and A. Chakravorty, unpublished results.

TABLE III
VARIABLE-TEMPERATURE MAGNETIC SUSCEPTIBILITY DATA IN
BENZENE FOR SOME NICKEL(II) COMPLEXES OF TYPE 1^a
(X = HALOGEN)

Compound			Temp, °K	μ_{eff} , BM	ΔH° , kcal mol ⁻¹	ΔS° , eu
R	X	M				
CH ₃	F	Ni	303	0.56	2.4 (±0.2)	1.5 (±0.7)
			313	0.59		
			323	0.65		
			333	0.66		
CH ₃	Cl	Ni	293	1.26	2.0 (±0.2)	3 (±1)
			303	1.35		
			313	1.40		
			323	1.45		
CH ₃	Br	Ni	294	1.39	1 (±0.3)	0.4 (±0.2)
			304	1.42		
			313	1.45		
			323	1.48		

^a Refer to compound figure number in the text.

TABLE IV
FREQUENCIES (ν , cm⁻¹) AND EXTINCTION COEFFICIENTS (ϵ ,
M⁻¹ cm⁻¹) OF ELECTRONIC BANDS OF COBALT(II) COMPLEXES
OF TYPE 1^a IN SOLID PHASE AND IN BENZENE SOLUTION AT
ROOM TEMPERATURE (300–303 °K)

Compound			Solid	Benzene soln ^b
R	X	M		
CH ₃	F	Co	9090, 15,870, 20,000	8130 (27), 9900 (24), 13,890 (8), 15,870 (14), 21,280 (470), 25,000 (2190) ^c
			CH ₃	Cl
CH ₃	Br	Co	6800, 11,240, 13,890, 15,630, 18,180, 20,400	7410 (31), 10,200 (21), 13,890 (3), 15,630 (4), 21,280 (320) ^c
			CH ₃	I
CH ₃	OCH ₃	Co	9180 ^d	7940 (26), ^d 14,290 (2), ^c 20,000 (318) ^c
CH ₃	OC ₂ H ₅	Co	ϵ	7940 (25), ^d 20,410 (362) ^c
CH ₃	SCH ₃	Co	8480, 10,530, 16,130	8200 (16), 10,530 (16), 20,000 (770) ^c

^a Refer to the compound figure number in the text. ^b Solute concentrations were adjusted as to get the optical density values generally in the range 0.5–1. ^c Shoulder. ^d Center of a broad asymmetric band. ^e Spectral measurements not made.

parently merge together forming a single broad band (Figure 1). The mull spectrum of the iodo complex, (CH₃I)₂Co, is completely different with bands at 11,600 and 15,600 cm⁻¹. However, in benzene solution its spectrum is akin to those of the chloro and bromo analogs (Figure 2); all the three complexes show two overlapping features in the frequency range 6300–12,500 cm⁻¹. The separation between these two features increases in the order Cl < Br < I. One further observation is that for a given complex the separation in the crystalline state is larger than in the solution phase.

Another important region of absorption in the (RX)₂Co complexes is 16,600–25,000 cm⁻¹. One or more bands can be seen in Nujol mull (Table IV). In the solution phase these appear in the form of shoulders on a steeply rising ultraviolet tail.⁷

Spectra of (CH₃OCH₃)₂Ni taken in Nujol mull and in benzene solution are shown in Figure 3. There are at least two bands under the broad feature in the near-ir region (6600–10,000 cm⁻¹). The absorption in the

(7) The first π - π^* transition in triazine 1-oxides and its chelates lies in the region 28,000–32,000 cm⁻¹.

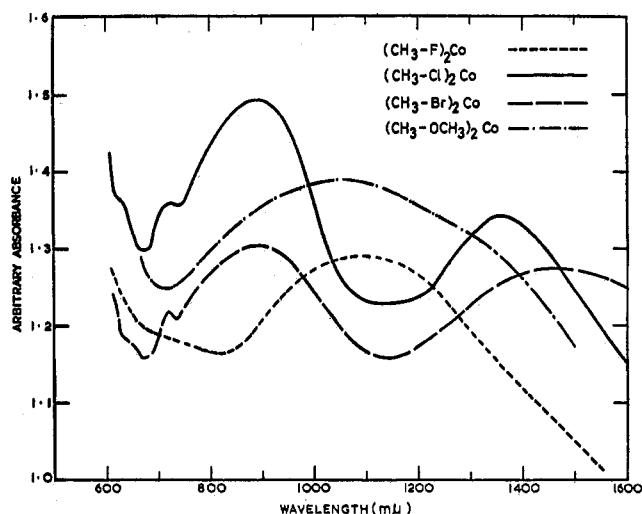


Figure 1.—Electronic spectra of some cobalt complexes in Nujol mull.

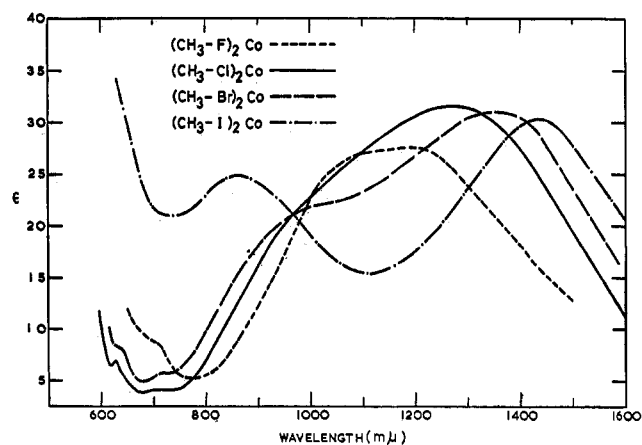


Figure 2.—Electronic spectra of some cobalt complexes in benzene.

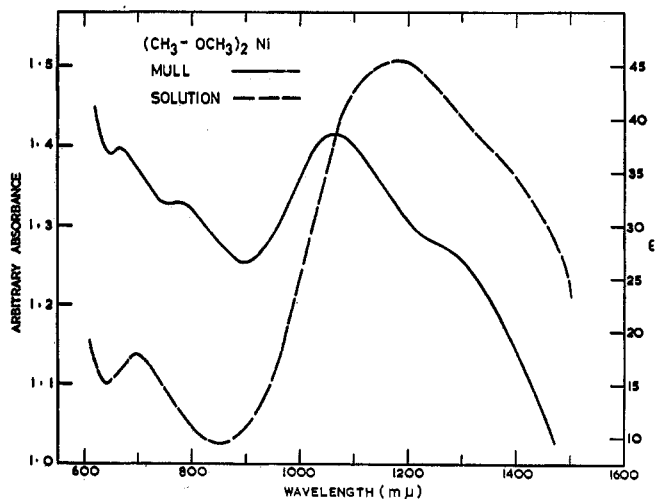


Figure 3.—Electronic spectra of one nickel complex in Nujol mull and in benzene.

region 12,500–16,600 cm⁻¹ is also multicomponent. The other fully paramagnetic nickel(II) complexes behave similarly (Table V).

More interesting is the case of the (RX)₂Ni complexes having X = halogen.⁸ In the crystalline state these

(8) Preliminary communication: P. S. Zacharias, B. Behera, and A. Chakravorty, *J. Amer. Chem. Soc.*, **90**, 7363 (1968).

TABLE V

FREQUENCIES (ν , cm^{-1}) AND EXTINCTION COEFFICIENTS (ϵ , $M^{-1}\text{cm}^{-1}$) OF ELECTRONIC BANDS OF COMPLETELY PARAMAGNETIC NICKEL(II) COMPLEXES OF TYPE 1^a IN SOLID PHASE AND IN BENZENE SOLUTION AT ROOM TEMPERATURE (300–303°K)

Compound			Solid		Benzene soln ^b	
R	X	M				
CH ₃	OCH ₃	Ni	7690, ^c 9440, 12,660, 14,700	8550 (47), ^d 14,390 (18), 20,000 (240) ^c	14,390 (18), 20,000	
CH ₃	OC ₂ H ₅	Ni	7630, ^c 9260, 12,820, 14,700	7140 (36), ^c 8480 (50), 14,490 (22), 20,410 (230) ^c	8480 (50), 14,490	
CH ₃	SCH ₃	Ni	9900, ^d 14,710 ^d	6670 (25), ^c 9900 (75), 15,150 (28), 18,520 (46) ^c	9900 (75), 15,150	
C ₂ H ₅	OCH ₃	Ni	<i>e</i>	8480 (50), ^d 14,700 (21), 20,000 (260) ^c	14,700 (21), 20,000	
C ₂ H ₅	OC ₂ H ₅	Ni	<i>e</i>	7140 (33), ^c 8930 (51), 14,390 (23), 20,000 (200) ^c	8930 (51), 14,390	
<i>n</i> -C ₈ H ₇	OCH ₃	Ni	<i>e</i>	7140 (34), ^c 8550 (45), 14,490 (19), 20,000 (300) ^c	8550 (45), 14,490	

^a Refer to the compound figure number in the text. ^b Solute concentrations were adjusted as to get the optical density values generally in the range 0.5–1. ^c Shoulder. ^d Center of a broad asymmetric band. ^e Spectral measurements not made.

diamagnetic chelates show a single well-defined feature at $\sim 13,800\text{ cm}^{-1}$. However, in the solution phase they show two distinct regions of absorption (Figure 4,

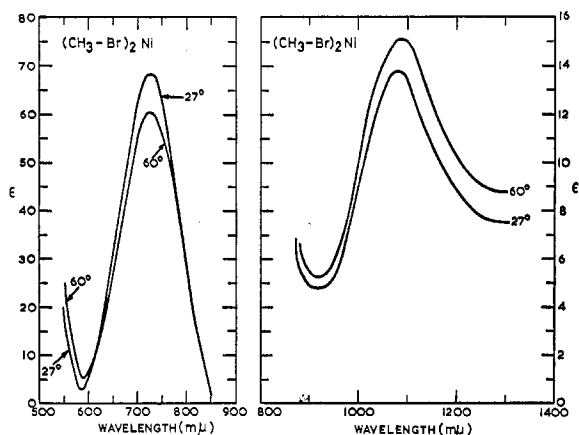


Figure 4.—Temperature dependence of the electronic bands of one nickel complex in benzene.

Table VI): one at $\sim 13,800\text{ cm}^{-1}$ and the other at $\sim 9000\text{ cm}^{-1}$. The latter band has a shoulder at lower energy.

TABLE VI

FREQUENCIES (ν , cm^{-1}) AND EXTINCTION COEFFICIENTS (ϵ , $M^{-1}\text{cm}^{-1}$) OF ELECTRONIC BANDS OF PARTIALLY PARAMAGNETIC NICKEL(II) COMPLEXES OF TYPE 1^a IN BENZENE AT ROOM TEMPERATURE (300–303°K)

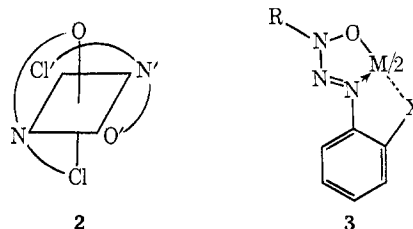
Compound			Benzene solution ^b	
R	X	M		
CH ₃	F	Ni	8930 (2), ^c 13,790 (98), 20,830 (190) ^d	
CH ₃	Cl	Ni	9090 (11), ^c 13,790 (78), 20,410 (150) ^d	
CH ₃	Br	Ni	9270 (15), ^c 13,790 (74), 20,830 (160) ^d	
CH ₃	I	Ni	9350 (7), ^c 13,890 (79), 20,000 (95) ^d	
CH ₃	H ^e	Ni	13,600 (108), 20,410 (200) ^d	
CH ₃	H ^f	Ni	13,500 (110)	

^a Refer to the compound figure number in the text. ^b Solute concentrations were adjusted, as to get the optical density values generally in the range 0.5–1. ^c It has a shoulder in the lower energy region. ^d Shoulder. ^e OCH₃ group in the 3 position of the benzene ring in 1.^a ^f Cl group in the 3 position of the benzene ring in 1.^a

Discussion

Structure of Cobalt(II) Chelates in the Crystalline State.—The structure of one chelate, *viz.*, $(\text{CH}_3\text{Cl})_2\text{Co}$,

has been accurately determined by three-dimensional X-ray diffraction.^{9,10} The crystal consists of discrete molecules of $(\text{CH}_3\text{Cl})_2\text{Co}$. The nearest neighbors to the metal atom are O, N(3), and Cl, the distances (in Å) being as follows: Co–O, 1.998 (13); Co–O', 1.985 (13); Co–N, 2.012 (14); Co–N', 1.980 (14); Co–Cl, 2.943 (7); Co–Cl', 3.016 (7). The primed and unprimed sets refer to the two ligands (2). A few selected angles (in degrees) at the metal atom are as follows: OCoCl, 146.7; OCoN', 111.4; OCoCl', 85.4; Cl'CoO', 145.0; OCoN, 78.6; NCoN', 153.0; OCoO', 122.6; ClCoO', 84.5. The Co–O and Co–N distances are normal. Metal–chlorine distances, in those cases where the *chloride ion* is known to occupy a pseudooctahedral coordination position around cobalt(II), usually lie¹¹ in the range 2.4–2.5 Å. The average Co–Cl distance in the present complex is $\sim 20\%$ larger than this. However, it is significant that the chloro groups are in proper positions to complete a highly distorted octahedral coordination sphere around cobalt(II) and a weak metal–chlorine bonding undoubtedly exists. A chloro group (attached to an aryl or alkyl group), unlike the chloride ion, will normally be considered a very poor donor and no previous example¹² is known to us in which this group has been shown to occupy a definite coordination position in the solid state and in the solution phase (*vide infra*). The relatively large Co–Cl distance in the present complexes probably results both from the weak donor character of the chloro group and the steric requirements of the ligand which is meridionally (2) disposed. Molecular models show facial dispositions to be sterically highly unfavorable.



The X-ray diffraction work⁹ has also shown that $(\text{CH}_3\text{Cl})_2\text{Co}$ is correctly formulated as a triazene 1-oxide chelate (*i.e.*, structural type 1) rather than a hydroxy-triazene chelate (structural type 3). Infrared data of some free ligands have led to the same conclusion previously.^{8,13} Electronic spectra and magnetic moments of the remaining cobalt(II) chelates (except X = I) are closely parallel to those of $(\text{CH}_3\text{Cl})_2\text{Co}$. It is therefore inferred that all these chelates uniformly

(9) G. L. Dwivedi and R. C. Srivastava, *Acta Crystallogr.*, in press.

(10) The only other reported crystal and molecular structure of a triazene 1-oxide chelate appears to be that of bis(1,3-diphenyltriazene 1-oxide)-palladium(II). This complex has the expected trans-planar arrangement: E. F. Meyer, Jr., *Diss. Abstr.*, **26**, 1368 (1965).

(11) Examples are as follows: *trans*-Co(py)₂Cl₂ (Co–Cl = 2.32 Å), M. A. Porai-Koshits and A. S. Antsyshikina, *Dokl. Akad. Nauk SSSR*, **92**, 333 (1953); Co(py)₂Cl₂ (2.49 Å), J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957); CoCl₂·6H₂O (2.43 Å), J. Mizuno, *J. Phys. Soc. Jap.*, **15**, 1412 (1960); Co(AlCl₄)₂ (2.47 Å), J. A. Ibers, *Acta Crystallogr.*, **15**, 967 (1962); CoCl₂·2H₂O (2.47 Å), B. Morosin and E. J. Graeber, *ibid.*, **16**, 1176 (1963); *trans*-Co(tu)₂Cl₂ (2.469 Å), J. E. O'Connor and E. L. Amma, *Inorg. Chem.*, **8**, 2367 (1969).

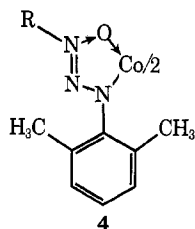
(12) Solution epr studies have indicated that chloroform can coordinate to copper(II) in its β -diketonato complexes: S. Antosik, N. M. D. Brown, D. A. McConnell, and A. L. Porte, *J. Chem. Soc. A*, 545 (1969). However, the structural situations in these cases are quite different from what we are concerned with in this paper.

(13) T. Mitsuhashi, Y. Osamura, and O. Simamura, *Tetrahedron Lett.*, 2593 (1965).

belong to the same structural type, 2, in which the X group occupies a coordination position.

In what follows we shall describe and then discuss the magnetic and spectral characteristics of 1 in terms of a pseudooctahedral model. The possibility of interpreting the results using a model in which the M-X interactions are ignored will be considered next.

Magnetic Behavior of the Complexes.—The observed magnetic moments (Table II) of all but $(\text{CH}_3\text{I})_2\text{Co}$ lie in the range expected for distorted octahedral stereochemistry.¹⁴ The moment of $(\text{CH}_3\text{I})_2\text{Co}$ is 2.13 BM in the crystalline state (Table II). This moment falls in the same range as that of several other triazene 1-oxide chelates (e.g., 4) which apparently have¹⁵ a grossly planar geometry. The electronic spectrum of crystalline $(\text{CH}_3\text{I})_2\text{Co}$ is very similar to that¹⁵



of 4 but is quite different from those of other $(\text{CH}_3\text{X})_2\text{Co}$ species described in this paper. These observations lead us to conclude that $(\text{CH}_3\text{I})_2\text{Co}$ exists essentially in the planar form in the crystalline state. In benzene solution, however, the room-temperature magnetic moment of $(\text{CH}_3\text{I})_2\text{Co}$ is 4.42 BM. This increase in magnetic moment on dissolution is ascribed to a change in geometry from planar ($S = 1/2$) to octahedral ($S = 3/2$). The latter is believed to involve iodo coordination. The solution moment (4.42 BM) is significantly less^{16,17} than those (Table II) of the other $(\text{CH}_3\text{X})_2\text{Co}$ complexes.

The fully paramagnetic nickel(II) complexes (Table II) are believed to have a pseudooctahedral geometry presumably of the same type as that of the cobalt(II) analogs. The case of the $(\text{CH}_3\text{X})_2\text{Ni}$ complex, having X = halogen, will be discussed separately in a later section of this paper.

Electronic Spectra.—High-spin cobalt(II) in O_h symmetry generally shows^{14,18} an absorption band in the near-ir region assignable to the transition ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1). We assign the two bands (6300–12,500 cm^{-1}) observed in the $(\text{RX})_2\text{Co}$ complexes to components of the parent ν_1 band which is split by the low

(14) R. L. Carlin, *Transition Metal Chem.*, 1, 1 (1965).

(15) P. S. Zacharias and A. Chakravorty, unpublished investigations.

(16) This may mean that there is a planar-octahedral equilibrium in solutions of the iodo complex. If this is true, the percentage of pseudooctahedral species existing in equilibrium is given by the relation

$$x = \frac{\mu_{\text{obsd}}^2 - \mu_p^2}{\mu_o^2 - \mu_p^2} 100$$

where μ_p and μ_o are the magnetic moments of the planar and the octahedral form, respectively, and μ_{obsd} is the observed magnetic moment. Substituting μ_{obsd} , μ_p , and μ_o by 4.4, 2.1, and 4.8 BM, respectively, the value of x is found to be 80.

(17) An alternative to the suggestion given in ref 16 is that the iodo complex is effectively less symmetric than the other halo complexes. This can lead to a decreased orbital contribution. A second alternative also dependent upon decreased orbital contribution is to invoke a pseudotetrahedral geometry (no iodo coordination). In fact, the observed moment of $(\text{CH}_3\text{I})_2\text{Co}$ falls ideally in the range expected¹⁴ for pseudotetrahedral cobalt(II) complexes. However, electronic spectral data are not in accord with such a proposition.

(18) J. Ferguson, D. L. Wood, and K. Knox, *J. Chem. Phys.*, 39, 881 (1963); W. C. Jones and W. E. Ball, *J. Chem. Soc. A*, 1849 (1968).

symmetry¹⁹ of the ligand field. Nothing is known about the position of the halo groups in the spectrochemical series. However, assuming that these are parallel to those of the halide ions, one may expect²⁰ that the splitting of the ν_1 band will increase in the order $\text{F} < \text{Cl} < \text{Br} < \text{I}$. This is observed in practice. Interestingly, the order of splitting in $(\text{CH}_3\text{OCH}_3)_2\text{Co}$ and $(\text{CH}_3\text{SCH}_3)_2\text{Co}$ is $\text{OCH}_3 < \text{SCH}_3$. Splitting of the ν_1 band due to low symmetry of the ligand field has been observed previously in, e.g., hexakis(pyridine 1-oxide)-cobalt(II) perchlorate²¹ and *cis*-(α -pic)₂Co(NO₃)₂ and related molecules.²² The point of special interest about the complexes under investigation is that they show a wide range of splitting varying systematically from member to member. The absorption in the 16,600–25,000- cm^{-1} region of the cobalt(II) complexes is reasonably assigned to the parent ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ (ν_2) transition. Last, one or two weak bands can be seen in the region 13,300–16,600 cm^{-1} (Figures 1 and 2). Whether these correspond to spin-forbidden transitions and/or to the two-electron ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ transition is not certain.

Coming to the nickel(II) complexes the bands in the region 6600–10,000 cm^{-1} are probably derived from the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (ν_1) transition²³ in O_h symmetry. The most likely origin of the 12,500–16,600- cm^{-1} absorption is the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ (ν_2) transition although the spin-forbidden ${}^3\text{A}_{2g} \rightarrow {}^1\text{E}_g$ excitation can also contribute to the intensity on the low-energy side. The ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ (ν_3) band is probably hidden under intense absorption in the ultraviolet spectrum.

Alternative Interpretation of Results. An Attempt.

—So far the discussion has been based on a pseudooctahedral model for the high-spin complexes. The known structure of $(\text{CH}_3\text{Cl})_2\text{Co}$ suggested this model. However, since the observed Co-Cl distance is relatively large, it is necessary to ascertain whether the data can be analyzed and understood better by ignoring the M-X interactions completely. In this description the complexes will have a highly distorted tetrahedral MN_2O_2 coordination sphere (*vide* angles at cobalt(II) in $(\text{CH}_3\text{Cl})_2\text{Co}$ structure).

The observed ranges of magnetic moments of various pseudooctahedral and pseudotetrahedral cobalt(II) complexes overlap considerably and a general stereochemical identification based on magnetic data alone is unlikely to be convincing. However, for *similar ligand systems*, the pseudotetrahedral geometry may be expected to have a lower magnetic moment than its

(19) $(\text{CH}_3\text{Cl})_2\text{Co}$ as it exists in the crystal lattice is completely devoid of symmetry (C_1). The effective symmetry (partially or completely averaged environment) for spectral purposes can in practice be higher. For example if the chelate rings are neglected and the $\text{CoN}_2\text{O}_2\text{Cl}_2$ coordination sphere is considered to be derived from a regular octahedron, the symmetry increases to C_{2v} . In this symmetry, T_{1g} and T_{2g} split into $\text{A}_2 + \text{B}_1 + \text{B}_2$ and $\text{A}_1 + \text{B}_1 + \text{B}_2$, respectively. It is interesting to note that whichever component of T_{1g} becomes the ground state in C_{2v} only two of the three transitions to the components of T_{2g} are electronically allowed: (i) $\text{A}_2 \rightarrow \text{A}_1$; $\text{A}_2 \rightarrow \text{B}_1$, y ; $\text{A}_2 \rightarrow \text{B}_2$, x ; (ii) $\text{B}_1 \rightarrow \text{A}_1$, x ; $\text{B}_1 \rightarrow \text{B}_1$, z ; $\text{B}_1 \rightarrow \text{B}_2$; (iii) $\text{B}_2 \rightarrow \text{A}_1$, y ; $\text{B}_2 \rightarrow \text{B}_1$; $\text{B}_2 \rightarrow \text{B}_2$, z .

(20) The implication is that the spectrochemical order will read as iodo < bromo < chloro < fluoro < O, N (triazene 1-oxide).

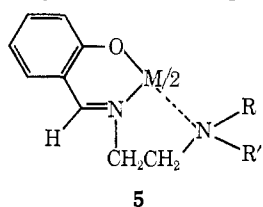
(21) W. Byers, A. B. P. Lever, and R. V. Parish, *Inorg. Chem.*, 7, 1835 (1968).

(22) A. B. P. Lever, *ibid.*, 4, 1042 (1965).

(23) Many examples of the splitting of nickel(II) bands due to low-symmetry (particularly tetragonal) crystal field components are known: L. Sacconi, *Transition Metal Chem.*, 4, 199 (1968); S. M. Nelson and T. M. Sheperd, *J. Chem. Soc.*, 3276 (1965); D. A. Rowley and R. S. Drago, *Inorg. Chem.*, 7, 795 (1968).

pseudooctahedral counterpart. At least two well-authenticated cases of pseudotetrahedral chelated CoN_2O_2 coordination spheres are known: salicylaldiminates²⁴ and β -keto aminates.²⁵ In these chelates, the magnetic moments invariably lie in the range 4.20–4.50 BM. In bis-pyridine adducts (presumably trans octahedral) of the salicylaldiminates the moment increases to 4.80 BM. The observed magnetic moments of the $(\text{RX})_2\text{Co}$ complexes are appreciably higher (Table II) than 4.5 BM and we suspect that this happens due to the effective coordination number being 6 (pseudooctahedron).

The number and position (but not intensity) of ligand-field bands in the near-ir and visible regions of pseudotetrahedral and pseudooctahedral cobalt(II) derived from similar ligands show considerable similarity. The apparent correspondences are ν_1 (O_h) and ν_2 (T_d); ν_2 (O_h) and ν_3 (T_d). A striking example is provided by the salicylaldimine complexes²⁶ of type 5.



Depending on the nature of R and R', the amine nitrogen may (cis pseudooctahedral) or may not (pseudotetrahedral) be coordinated to the metal atom. The pseudooctahedral species show split ν_1 bands at $\sim 9000\text{ cm}^{-1}$ ($\epsilon \sim 10$) and $\sim 12,000\text{ cm}^{-1}$ ($\epsilon \sim 10$) while the components of the pseudotetrahedral ν_2 bands are at 8000 cm^{-1} ($\epsilon \sim 60$) and $\sim 12,000\text{ cm}^{-1}$ ($\epsilon \sim 35$). The intensity in the $8000\text{--}12,000\text{ cm}^{-1}$ region of $(\text{RX})_2\text{Co}$ complexes are considerably lower than those of pseudotetrahedral salicylaldiminates but higher than those of pseudooctahedral salicylaldiminates. If the effective geometry of $(\text{RX})_2\text{Co}$ complexes is in fact pseudotetrahedral, the observed intensities will represent lowest values observed to date for complexes of this geometry thereby implicating an unusually high ionic character of the metal-ligand bonds.²⁷ On the other hand in a pseudooctahedral model, the relatively high intensity can be understood in terms of large distortions from O_h symmetry as is actually observed for the $(\text{CH}_3\text{Cl})_2\text{Co}$ complex. Coming to nickel(II) complexes, the spectrum of, e.g., $(\text{CH}_3\text{OCH}_3)_2\text{Ni}$ is strikingly similar to those of pseudooctahedral nickel(II) complexes²⁸ belonging to the structural type 5. Significantly, the intensity of the near-ir band follows the order nickel(II) > cobalt(II) for both type 1 and type 5 complexes. For tetrahedral complexes the reverse order is usually observed in salicylaldiminates,^{24, 29a} in β -keto aminates,^{25, 29b} and in general.³⁰

(24) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Amer. Chem. Soc.*, **84**, 3246 (1962); L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *ibid.*, **82**, 815 (1960).

(25) G. W. Everett, Jr., and R. H. Holm, *ibid.*, **88**, 2442 (1966).

(26) L. Sacconi, M. Ciampolini, and G. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).

(27) F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, **84**, 872 (1962).

(28) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

(29) (a) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Amer. Chem. Soc.*, **85**, 411 (1963); (b) G. W. Everett, Jr., and R. H. Holm, *ibid.*, **87**, 2117 (1965).

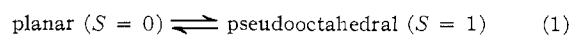
(30) A. B. P. Lever, "Inorganic Electronic Spectroscopy," American Elsevier, New York, N. Y., 1968, p 342.

The above observations taken collectively with the X-ray data on $(\text{CH}_3\text{Cl})_2\text{Co}$ lead us to believe that the crystal field due to the X groups observably affects magnetic and spectroscopic behavior of the present complexes which are therefore best described as pseudooctahedral in which the X group occupies a coordination position.

Solution Equilibria in $(\text{CH}_3\text{X})_2\text{Ni}$, X = Halogen.—These complexes are diamagnetic and hence grossly trans planar in the crystalline state. The band at $\sim 13,800\text{ cm}^{-1}$ is characteristic of this geometry.³¹ In the solution phase the $\sim 9000\text{ cm}^{-1}$ band clearly corresponds to the ν_1 band of $(\text{CH}_3\text{OCH}_3)_2\text{Ni}$. The band at $\sim 13,800\text{ cm}^{-1}$ shows that trans-planar species are simultaneously present. The octahedral ν_2 band is probably hidden under this absorption. Thus even a cursory examination of spectra shown in Figure 4 indicates the coexistence of planar and pseudooctahedral species in the solution phase. When the donor group X (e.g., Cl or OCH_3) is placed in the meta rather than in the ortho position (as in 1) of the benzene ring, the group, as expected, is no longer coordinated to the metal (Table VI).

The halo complexes are uniformly paramagnetic in benzene solution (Table III). However, the observed magnetic moments are very much less than 3.2 BM. The simplest interpretation of this result is that a diamagnetic conformation is heavily populated.

The spectral and magnetic results taken collectively lead us to suggest the existence of the equilibrium 1 in



these solutions. Temperature-dependent susceptibility measurements were carried out in order to characterize these equilibria thermodynamically (Table III). The immediate qualitative observation to make is that the paramagnetism *increases* with increase in temperature. There is a parallel increase in the intensity of the ν_1 band (Figure 4). All these changes are fully reversible with respect to temperature showing that we are dealing with a true equilibrium situation.

The constant K for the equilibrium 1 is related to magnetic moments by

$$K = \frac{[\text{pseudooctahedral}]}{[\text{planar}]} = \frac{\mu_{\text{eff}}^2}{\mu_0^2 - \mu_{\text{eff}}^2} \quad (2)$$

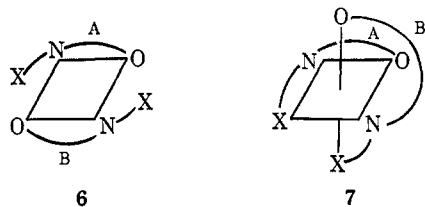
In (2), μ_0 is the magnetic moment of the pseudooctahedral species and μ_{eff} is the observed magnetic moment of the equilibrium solution. Values of ΔH° and ΔS° obtained as least-squares slopes and intercepts of the plot of $\log K$ vs. $1/T$ are shown in Table III.

The measured solution magnetic moments are relatively small (Table III; 0.5–1.5 BM) and are therefore subject to large experimental errors. One further disadvantage is that the change in magnetic moments over the temperature range accessible to us is not very large. Due to these factors the values of ΔH° and particularly ΔS° are subject to considerable experimental errors. For every compound measurements were carried out at least three times. The plots of $\log K$ vs. $1/T$ usually fell close to each other and were parallel. The thermodynamic parameters shown in Table III are arithmetic means of the three measurements for each case. The maximum deviation observed from the mean is shown

(31) B. Behera and A. Chakravorty, *Inorg. Chim. Acta*, **4**, 372 (1970).

in parentheses. It is best to consider the values of ΔH° and ΔS° to be of qualitative significance only.

One interesting observation is that ΔH° for the transformation planar \rightarrow octahedral is uniformly positive. This transformation can be represented as 6 \rightarrow 7. In the simplest model the conversion 6 \rightarrow 7 can be visualized as a two-step process: (1) the relative orientation of rings A and B changes; (2) two long Ni-X bonds are



formed. The change in geometry is also attended with a change in multiplicity of nickel(II). The first step may be expected to be endothermic.³² The second step is most likely to be exothermic. The observed sign of ΔH° shows that energetically the first step plays the dominant role. This is not surprising since the Ni-X bonds are likely to be very weak (on the basis of the known structure of $(\text{CH}_3\text{Cl})_2\text{Co}$). The sign of ΔS° can be rationalized along similar lines using the same model. We have not carefully examined the effect of varying the solvent on the position of equilibrium 1. However, spectral results suggest that it shifts to the right in going from benzene to chloroform.

Concluding Remarks

One general result of this research is that halo groups suitably attached to the aromatic ring of triazene 1-oxides can occupy a pseudooctahedral coordination position around cobalt(II) and nickel(II). The metal-

(32) The step (1) involves a distortion from a planar toward a tetrahedral NiN_2O_2 coordination. Planar \rightarrow tetrahedral conversions are usually endothermic. See for example: R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, **86**, 379 (1964); R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966); D. H. Gerlach and R. H. Holm, *J. Amer. Chem. Soc.*, **91**, 3457 (1969).

halogen bond, though weak, observably affects properties of these systems. The complexes deviate considerably from O_h symmetry and this is neatly reflected in electronic spectral data. In the case of nickel(II) complexes, the population of the octahedral configuration in the solution phase follows the order $F < \text{Cl} < \text{Br} \ll \text{OCH}_3 \sim \text{SCH}_3$. The iodo complex is too insoluble for reliable magnetic measurements. However, if the intensity of the $\sim 9300\text{-cm}^{-1}$ band is taken as an index of the population of the pseudooctahedral species, the above series may be completed for the halo groups: $F < \text{Cl} < \text{Br} > \text{I}$. In cobalt(II) complexes also the iodo group behaves differently. Probably the large size of the iodo group is a determining factor.

One further observation to make is that for a given ligand the extent of halo coordination follows the order cobalt(II) \gg nickel(II). Thus while $(\text{CH}_3\text{Cl})_2\text{Ni}$ shows an equilibrium in solution, the corresponding cobalt(II) complex exists essentially $\sim 100\%$ in the pseudooctahedral form. At least for this class of ligands the octahedral quartet state of cobalt(II) is populated with greater facility than the octahedral triplet state of nickel(II).³³

The behavior of nickel(II) complexes clearly demonstrates that ether and thioether groups are better coordinating agents than the halo groups. This is not unexpected. In fact the $\text{X} = \text{OCH}_3$, OC_2H_5 , and SCH_3 complexes were synthesized in order to establish the behavior in the 100% pseudooctahedral limit.

Acknowledgment.—Our sincere thanks are due to Dr. R. C. Srivastava for supplying advance information on the structure of $(\text{CH}_3\text{Cl})_2\text{Co}$. The grant of a Senior Research Fellowship to P. S. Z. by the Department of Atomic Energy, New Delhi, India, is gratefully acknowledged. Microanalyses were done by Mr. A. H. Siddiqui of this department.

(33) An interesting parallel to this is provided by the higher population of the tetrahedral configuration in the case of cobalt(II) compared to nickel(II) complexes of some Schiff bases: G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

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The Stereochemistry of Four-Coordinate Bis(methinodiphosphinate)metal(II) Chelate Complexes

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A series of bivalent metal complexes of the type $[\text{YP}(\text{C}_6\text{H}_5)_2\text{CHP}(\text{C}_6\text{H}_5)_2\text{Y}]_2\text{M}^{\text{II}}$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$; $\text{Y} = \text{S}, \text{Se}$) have been synthesized. The sulfur and selenium complexes of iron(II) and cobalt(II) are tetrahedral while the nickel(II) complexes are planar. The selenium complexes of iron(II) and cobalt(II) are the first examples of tetrahedral coordination of four seleniums to these metals.

Introduction

A large amount of comparative chemistry on four-coordinate metal(II) bis-chelate compounds¹ has produced some generalizations on their stereochemical behavior. (A) All nickel(II) complexes with donor

(1) R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, in press.

atoms which are not sterically hindered (*e.g.*, O, S, Se, NH donors) have been found to be planar. (B) For a given ligand backbone, the order of stabilization of planar *vs.* tetrahedral² forms in cobalt(II) complexes

(2) The chelate rings reduce the symmetry of the molecule from T_d to D_{2d} or lower; however, the local symmetry around the metal is tetrahedral.